

**A COMPARISON OF DEHYDRATION PROCESSES OF Al-, Fe<sup>2+</sup>-, & Mg-SULFATES UNDER MARS RELEVANT PRESSURES AND THREE TEMPERATURES.** Yuhang Zhou and Alian Wang, Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130, USA (yuhang@levee.wustl.edu) (alianw@levee.wustl.edu)

**Introduction:** Hydrous sulfates (Ca-, Mg-, Fe-sulfates, and recently Al-sulfates) have been found on Mars by OMEGA (Mars Express orbiter) [1], CRISM (Mars Reconnaissance orbiter) [2], the Spirit and Opportunity rovers [3], and Phoenix lander [4]. Furthermore, the change in hydration degree of Fe<sup>3+</sup>-sulfates after exposed to the current Martian atmospheric condition was suggested by long-duration repeating observations of the Spirit rover [5].

Laboratory experiments on the fundamental properties of hydrous sulfates would help us to link these mission observations to geochemical and hydrological processes that have happened at Martian surface or within the subsurface. A recent study reported the using of a set of dehydration experiments under Mars relevant atmospheric pressure (P), and partial water pressure (P<sub>H2O</sub>) to derive the dehydration half-life of epsomite (MgSO<sub>4</sub>·7H<sub>2</sub>O) at low temperature (T), and suggested a large amount of hydrous Mg-sulfates may still remain within the subsurface on Mars [6]. In this study, we conducted two sets of similar experiments on alunogen [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·17H<sub>2</sub>O] and melanterite [FeSO<sub>4</sub>·7H<sub>2</sub>O]; the two sulfates having the highest hydration degrees in their series. These two minerals were observed occurring at terrestrial geological setting, as precipitation products from aqueous solution at middle to low T. The purpose of our study is to compare their dehydration processes with that of epsomite. We report here the preliminary results of the experiments.

**Samples and Experiments:** The starting materials, alunogen [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·17H<sub>2</sub>O] and melanterite [FeSO<sub>4</sub>·7H<sub>2</sub>O], were hand grounded and sieved to 90 - 150 μm grain size to ensure sufficient surface area for reaction. The sample powder was put into a humidity buffer jar filled with KNO<sub>3</sub> solution (~94% relative humidity [RH] at room T) for a few days to re-gain the highest hydration degree. 100 Raman spectra were taken on each of the two powder samples to confirm their identity and homogeneity before the start of ex-

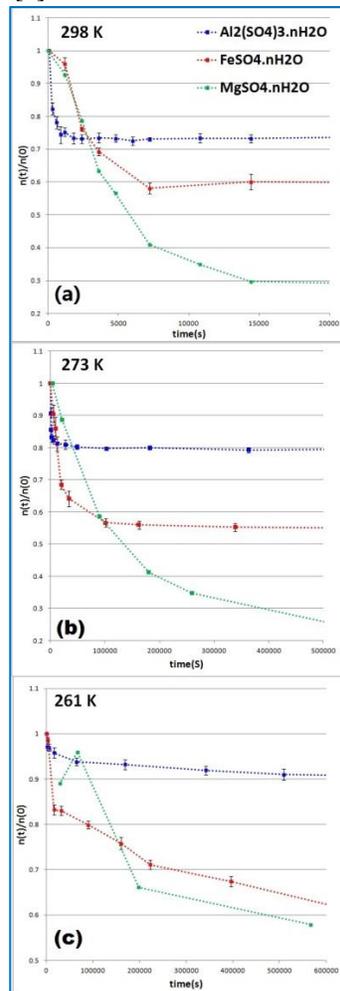
periments. For each experiment at a certain temperature (e.g., alunogen dehydration at 25 °C), 15 samples (each 60±5 mg for alunogen, each 120±5 mg for melanterite) were placed in reaction vials which were inserted in a vacuum desiccator.

The dehydration experiments were conducted in a vacuum desiccator, in which the atmospheric pressure (0.16 to 0.26 mbar) was maintained by a vacuum pump (slightly lower than average P<sub>Mars</sub> ~ 7 mbar) and monitored by a gas-pressure meter. Based on measured laboratory RH during the experiment period, the P<sub>H2O</sub> in vacuum desiccator calculated was in the range of 0.14 - 0.25 Pa (in the slightly higher range of P<sub>H2O</sub> on Mars ~ 0.04 - 0.15 Pa). For each of alunogen or melanterite sample, 3 experiments at 25°C, 0°C and -12°C were conducted. The selection of T range was based on a compromise between Mars' surface temperature range at equatorial region (e.g., -88 °C to 22 °C measured by Spirit and Opportunity) and the need to have a reasonable reaction rate in our experiments. The temperature of desiccator and the sample vials was kept at 25±1 °C on lab-bench, at 0±0.3 °C when immersed in an ice-H<sub>2</sub>O mixture, at -12±0.5 °C when placed in a T-controlled freezer.

During each experiment at a T, 10 sample vials were taken out at regular time intervals and gravimetric measurements (A Citizon<sup>R</sup> balance with resolution 0.1 mg) were made on them each time for monitoring the dehydration processes. The other 5 sample vials were taken out at a few selected time intervals to make noninvasive

microbeam Raman measurement (KOSI HoloLab 5000) for phase identifications. XRD measurements of final products provided clarification on the structural changes suggested by their Raman spectra.

The experimental durations are 26, 141, and 210 hours for alunogen dehydration at 25 °C, 0 °C and -12 °C, and 102, 238, and 174 hours for melanterite dehydration at 25 °C, 0°C and -12°C. The experiments were stopped when the mass change during a long time interval (e.g. 24 hours) being approximately zero.



**Figure 1 Comparison of dehydration processes of Al-, Fe-, and Mg-sulfates at 3 temperatures**

**Dehydration processes monitored by gravimetric measurement:** A 0.1 mg uncertainty in gravimetric measurement would correspond an uncertainty of 0.36% in calculation of the number of structural H<sub>2</sub>O per alunogen molecule (60±5 mg net mass per sample). Similarly, it corresponds an uncertainty of 0.16% in calculation of the number of structural H<sub>2</sub>O per melanterite molecule (120±5 mg net mass per sample). The results from gravimetric measurements for six experiments are plotted in Figure 1, as n(t)/n(0) (%) vs. time duration of experiment (second), where n(t) is the number of structural H<sub>2</sub>O per molecule (alunogen or melanterite) at a time (t) and n(0) is the same value at the beginning of experiment. n(0)=17 and 7 were used for alunogen and melanterite respectively. Data were plotted as mean values and standard deviations based on the measurements of 10 reaction vials at each time interval. The data from similar experiments of epsomite were also plotted for comparison.

Figure 1 first reveals the very different dehydration pathways among alunogen, melanterite, and epsomite. Alunogen dehydrated very fast at the beginning and then maintained an almost constant hydration degree (at 12.5 H<sub>2</sub>O per molecule in the experiments at 25 °C). Melanterite loss its H<sub>2</sub>O slowly and gradually then reached a stable hydration degree (e.g., at 4.3 H<sub>2</sub>O per molecule in the experiments at 25 °C). Epsomite dehydrated at a similar slope as melanterite did at the early stage (in the experiments at 25 °C) but continued to reach a much deeper dehydration (decreased from 7 to ~ 2.0 H<sub>2</sub>O per molecule in the experiments at 25 °C and 0 °C).

Figure 1 also reveals that, very similar to epsomite, the dehydration of both alunogen and melanterite are strongly dependent on temperature. At lower temperatures, not only the percentage of lost structural water is lower (10% at -12 °C while ~ 25% at 25 °C), but also the dehydration process took a much longer time (e.g., 210 hours at -12 °C compared with 26 hours at 25 °C for alunogen).

**Structural changes revealed by laser Raman spectroscopy:**

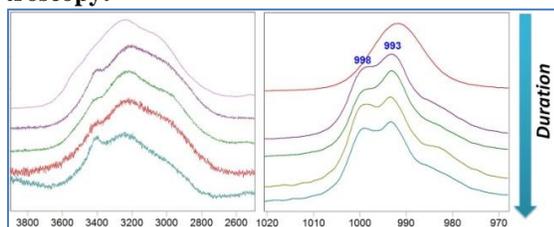


Figure 2 Raman spectra of  $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $n = 17$  to  $12.5$ ) during its dehydration at 298 K. H<sub>2</sub>O modes in left; SO<sub>4</sub> modes in right.

**Alunogen to meta-alunogen:** The symmetric stretching vibrational ( $\nu_1$ ) mode of the sulfate (SO<sub>4</sub>) of alunogen contributes a Raman peak at 993 cm<sup>-1</sup>. The right panel of Figure 2 shows an extra peak at 998 cm<sup>-1</sup> that appeared soon after the beginning of experiment,

accompanied by the appearing of 3406 cm<sup>-1</sup> peak and a general reduction of spectral signal to noise ratio in left panel of Figure 2. XRD measurement of the final product suggests meta-alunogen ( $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ ) has been formed. The number of structural H<sub>2</sub>O in this structure is consistent with the result of gravimetric measurement (Fig. 1, 298K), 12.5 H<sub>2</sub>O per alunogen molecule in the final stage of experiment at 298K is correspond to 12 H<sub>2</sub>O in meta-alunogen.

**Melanterite to rozenite:** The strongest Raman peaks ( $\nu_1$  mode of SO<sub>4</sub>) of melanterite [ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ], rozenite [ $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ] and szomolnokite [ $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ] occur at 976cm<sup>-1</sup>, 990cm<sup>-1</sup> and 1018 cm<sup>-1</sup> respectively [7]. In the right panel of Figure 3, during the early stages of dehydration experiments, the appearing 990 cm<sup>-1</sup> peak of rozenite indicates a mixture of melanterite and rozenite have formed. When dehydration developed, 990 cm<sup>-1</sup> peak of rozenite became dominant. 1014 cm<sup>-1</sup> peak of szomolnokite only occur at the final stage (102 hours) in the experiments at 25 °C, but not appeared in any of the experiments at 0°C and -12°C. The Raman peaks from H<sub>2</sub>O modes (left panel of Figure 3) experienced a similar variation, from a peak at 3435 cm<sup>-1</sup> with 3 shoulders, to a doublet at 3435 cm<sup>-1</sup> and 3380 cm<sup>-1</sup>, and to a single peak at 3435 cm<sup>-1</sup>. In addition, the spectral signal to noise ratio decreases following the development of dehydration. These Raman spectral features are consistent with the results of gravimetric measurement (Fig. 1, 298K), e.g., a dominate 990 cm<sup>-1</sup> peak of rozenite [ $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ] from the final product of experiment at 298K corresponds well with the 4.3 H<sub>2</sub>O per molecule based on gravimetric measurement.

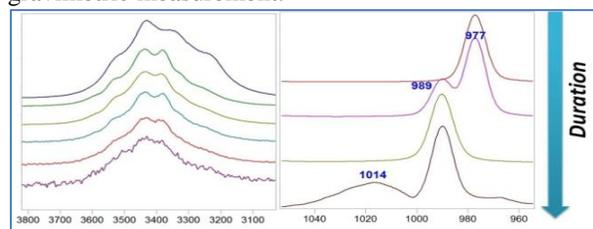


Figure 3 Raman spectra of  $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$  ( $n = 7, 4, 1$ ). H<sub>2</sub>O bending modes change at 298 K (left); characteristic SO<sub>4</sub> modes (right).

**Summary:** The differences in the bonding strength among structural H<sub>2</sub>O and polyhedral in the crystal structures of alunogen, melanterite, and epsomite are the causes for their different dehydration pathways. Detailed analyses will be developed and to be presented at the conference.

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**References:** [1] Bribing et al., 2006, *Science* Vol 312. P400-404; [2] Murchie et al., 2009, *JGR*; [3] Clark et al., 2007, *J. Geophys. Res.*, 112, E06S01; [4] Samuel, et al., 2010, *GRL*, VOL. 37, L09201; [5] Wang, A., and Z. C. Ling, 2011, *J. Geophys. Res.*, 116, E 00 F17; [6] Wang, 2012, #2172; *LPSC*; [7] Chio et al., 2006, *LPS XXXVII*.